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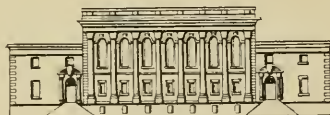
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GAS CHROMATOGRAPHY: THE INVESTIGATION OF A NEW ACTIVE ADSORBENT

by

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INTRODUCTION

Purpose:

At the beginning of the twentieth century Chromatography was a newly developed separation technique limited to colored substances. Since that time, extensive research has led to tremendous advances in both the theory and technology of Chromatography. As a result, this area of study today involves a variety of systems, of applications, and of possibilities for further investigation. In the fifties and early sixties Gas-Liquid Chromatography (GLC) was the subject of more concentrated interest than the older system of Gas-Solid Chromatography (GSC). In the last decade however, the search for more efficient and selective systems has aroused new interest in GSC. With this in mind, it seems reasonable and advantageous to investigate experimentally the use of a solid, which has certain characteristics particularly suitable to GSC, as a possible stationary phase in this type of instrumentation.

The Philadelphia Quartz Company has recently produced a new family of silicas called Quso that have different structures, and as a consequence, different properties from other silicas. Micro fine Quso silica consists of very nearly spherical particles of low porosity and high available external surface area (325 sq. meters/gram). This product is more adsorptive than most silicas

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or silica gels and has a fully hydroxylated surface. Aside from the loss of free and hydrogen-bonded water which leaves silanol groups at the surface, Quso is stable at temperatures below 200° C.¹

In this paper the chromatographic value of Quso in GSC is discussed. This presentation is based on an experimental study with Quso, as well as a relevant practical and brief theoretical study of Gas Chromatography (GC) per se. In support of the selected topic and to provide the background and scope for a basic understanding of the subject, a review of GC history is included.

Chromatographic Methods:

Chromatography encompasses an assortment of methods which are all based on a similar separation phenomenon. A two-phase system is set up, one stationary and the other mobile. The substances to be separated are in equilibrium or distribute themselves between the two phases. Due to differences in structure, one substance may remain in (or on) the stationary phase longer than another substance. If the distribution of the mixture is reestablished a number of times as the mobile phase transports the mixture over or through a column of the stationary phase, the substances will eventually be separated into zones or .

bands.* After a certain length of time, the component that is least strongly held appears at the greatest distance from the initial point of introduction.

Chromatography is divided into several categories according to the physical nature of the two phases and therefore, the equilibrium or partitioning taking place: Liquid-Solid (LS), Liquid-Liquid (LL), Gas-Solid (GS), Gas-Liquid (GL), and Gas-Solid-Liquid (GSL).

In GC the moving phase is the carrier gas. The sample is introduced as a vaporized liquid, gas, or vaporized solid; and the carrier gas transports it through a column containing the stationary phase. The stationary phase may be a solid adsorbent or a nonvolatile liquid coating on an inert support. In some cases the walls of the column are used as the inert support, but commercially prepared granular supports such as Chromosorb P or W are more common.

The specific analysis technique employed in GC may be elution, frontal, or displacement. In the elution technique, a

*The theory which regards the column as a discontinuous medium, built up of a large number of equivalent plates where equilibrium is successively achieved, is referred to as the plate concept. Actually since one phase is continuously moving (in GC especially where the flow rate is large), complete equilibrium is never fully realized.² The height equivalent to a theoretical plate (HETP) is the length of the column (L) divided by the number of plates in the column (n). n is calculated from the equation $n = 16(d_R/y_d)^2$ where d_R is the retention distance from sample injection to maximum peak height on a chromatogram, and y_d is the peak width.³ The size of the HETP term is an indication of the efficiency and resolution to be obtained with a particular column.

distinct sample mixture is introduced into the column and repeatedly partitions itself between the phases. The components move through the column at different rates and emerge from it at different times. In frontal analysis a continuous stream of carrier gas and sample at a constant initial concentration is employed. The least strongly retained component saturates the column and passes out with just carrier gas; while the second and subsequent components emerge contaminated with previous components that have been retarded to a lesser degree. Instead of the usual Gaussian peaks in gas elution, a differential detector gives a step pattern.^{4*} Little investigation with this technique has been conducted due to the contamination of separated sample components and the competition for adsorption sites involved in the process. This competition is believed to affect the sensitivity of the method.

Likewise, in gas displacement, relatively little work has been done because of the sorptive competition present.⁵ A desorbent displaces the most strongly held solute from the stationary phase, which displaces the next most strongly held one, et cetera. The end result is that the components emerge in least-to-most-strongly adsorbed order.⁶ The chromatogram from a concentration-sensitive detector might show a series of steps.

* A recorder receives an electrical signal from the detector, and in turn records on chart paper a graphic representation of the concentration of the sample in the carrier gas.

If a thermal conductivity cell is used as the detector, components emerging consecutively and having similar thermal conductivities may not be distinguishable.⁷

The chromatographic method is similar to both distillation and extraction for the methods also follow the same principle of forming a two phase system from a one phase system followed by the subsequent separation of the phases. All share the concept of equilibrium between phases, and all three usually result in improved separation by repeating this equilibrium step. However, in distillation and extraction the two phases move in opposite directions in the equipment. A countercurrent operation exists that is not present in GC, or chromatography in general. Other differences arise from the facts that in distillation and countercurrent extraction both phases are actually moving and the processes may be made continuous, while chromatography has only one mobile phase and is always a batch process.⁸

History:

Gas Chromatography has its origin in the early chromatographic techniques of separation utilized by biologists at the beginning of the twentieth century. M. Tswett, a Russian botanist, is credited with publishing the first paper on column chromatography in 1906. Green chlorophyll and yellow carotenoid pigments extracted from leaves were dissolved in a petroleum ether solution

and filtered through a glass tube containing powdered calcium carbonate. As more pure solvent was poured down the column, the pigments separated into selective zones of the column.⁹ At this time the term chromatography was applied and, literally translated, it means color writing. The name may have been suggested by Tswett's colored solute column bands, but it is interesting to note as well that in Russian the name Tswett means color.¹⁰ Today the form of chromatography described by this botanist is called liquid-solid elution chromatography.

Not until after 1931 were the applications of chromatography widely realized. Kuhn, Lederer, and Winterstein separated carrot carotene and egg yolk xanthophyll into their isomeric components on a preparative scale on an alumina (Al_2O_3) and calcium carbonate column.¹¹ Carotene was thought to be a single compound until it was chromatographically separated into its three isomeric forms (α , β , γ). In a study of azo dyes Hartley accidentally performed the separation of cis and trans azobenzene on a chromatographic column. The separation of these stereoisomers had not been previously achieved.¹² In 1938 Reichstein introduced the flowing chromatogram in which filtrates of even colorless substances could be collected separately by washing the column with a series of solvents of continuously stronger eluting power. Tiselius contributed the techniques of frontal and displacement analysis over the years 1940-1943.¹³ He used an optical system to measure

changes in refractive index due to concentration changes in solutions passing through a packed column.¹⁴ In 1941 Martin and Synge found that partition isotherms (concentration in stationary phase vs. concentration in mobile phase) were more linear for distributions of solutes in liquid-liquid systems than in liquid-solid systems.* Although the idea of advantageously replacing the flowing liquid by gas was pointed out in their original paper, the immediate impact of their work proceeded from the discovery by Consden, Gordon, and Martin that paper strips could be employed in place of columns. Paper Chromatography became a powerful tool of both organic and biochemists, while experimentation in elution Gas Chromatography waned for another ten years. In 1952 James, in collaboration with Martin described the first account of this method. Following their initial report of success, Gas Chromatography developed at a remarkable pace.¹⁶ Today the literature contains thousands of papers on analyses utilizing this particular technique which is little more than fifteen years in age.

OPERATION

Apparatus:

A laboratory gas chromatograph for general purposes consists

* Ideally the slope of the curve [i.e. the partition coefficient $k = \text{conc (stationary phase)} / \text{conc (mobile phase)}$] should be constant over the entire concentration range to eliminate tailing.¹⁵ See page 12.

of four basic components: (a) the carrier gas supply and flow control, (b) the sample port or means of sample introduction, (c) the column, and (d) the detector.¹⁷

The type of detector in the instrument may vary according to the sensitivity required in an operation. Simple forms of thermal conductivity cells permit detection of parts per million concentrations of impurities whereas elaborate ionization detectors may be sensitive to the parts per billion level.¹⁸ Thermal conductivity cells are often used because of their versatility, and inherently high stability and signal-to-noise ratio. Two thermistors are employed as identical resistance elements in a Wheatstone Bridge.¹⁹ A reference element is exposed only to carrier gas and the second element, only to column effluent. When a mixture having a different thermal conductivity from the pure carrier gas passes over the detector unit, the rate of heat loss changes, and therefore the resistance of the second element, due to its subsequent temperature change. Owing to the opposition of the two resistance elements, the unbalanced bridge sends the recorder a differential signal, which is a function of the instantaneous concentration of the components in the carrier gas. If no component is present in the carrier gas, the two sides of the detector cooled by the gas are in balance and a stable baseline is recorded.

The carrier gas for thermal conductivity cells is usually an

inert gas with a thermal conductivity greatly different from the samples to be analysed. For reasons of lower viscosity and faster transfer of sample components in the gas phase, a gas of low molecular weight is employed.

Gas chromatographs or vapor fractometers, as they are sometimes called, may be modified or refined to meet the needs of the researcher, but they generally operate in the following fashion. From an external tank of compressed gas, the carrier gas passes through a pressure reducing valve, which controls the input pressure on the column, and on through the reference side of the detector to the sample port. Gradual changes in the carrier gas due to impurities present or temperature variation, which would be sensed by differential type detectors are compensated by having a reference side in opposition to the sensing side of the detector.²⁰ At the sample port, in an example of liquid sample introduction, a hypodermic syringe is used to inject a small amount of liquid (several microliters or less in size) through a self-sealing silicone rubber septum into the heated port. There, it is quickly vaporized and then swept with the gas into the column. After passing through the column, the mixture of carrier gas and sample components enters the sensing side of the detector which signals the recorder. The detector, column, and sample port are encased in a thermostatically-controlled jacket.

The temperature of the sample injection block must be high

enough to insure complete vaporization of the liquid introduced. The temperatures of the column and detector are usually equal and somewhat lower than that of the sample port. If the temperature of the detector is not at least that of the column, inadvertent condensation of the solute and a resulting change in concentration of gas mixture may occur. Since the detector is sensitive to concentration, an erroneous signal is provided.²¹

A moving bubble meter may be connected to the column outlet to measure the flow rate of gas emerging from the column. This can be a simple construction of a burette filled with a small amount of liquid soap solution. Adjacent to the burette is a U-tube to prevent the back flow of soap into the column.

Column Theory; Gas-Solid Elution Chromatography:

The column is referred to as "the heart of a gas chromatograph," since the success of any separation is largely dependent on its construction.²² In laboratory practice, four main factors are to be considered in evaluating the worth of any column:

(a) minimum height of column equivalent to a theoretical plate (HETP) and maximum number of theoretical plates (n) for efficiency purposes, (b) peak symmetry, (c) peak resolution, and (d) speed. In practice, these objectives can not be independently optimized. Varying certain parameters such as temperature, gas velocity, sample size, support surface area and particle size, packing,

column length and pressure drop affects the column effectiveness in dissimilar ways. Nevertheless, a compromise in which individual parameters are varied and optimized with respect to the overall optimum performance of the procedure can be reached.

The column packing may take a variety of forms according to the system (GLC, GSC, et cetera) to be used, and therefore the theories describing these systems are different. In evaluating an active adsorbent as a column stationary phase, it is of value to consider in some detail the theoretical approach to gas adsorption chromatography.

GSC is based on a particular property of solids, that of holding molecules at their surfaces. Porous and finely divided materials are especially marked by this property of adsorption. Both physical forces such as van der Waals forces and chemical forces involving chemical bonds can participate. Differences in "adsorbability" of sample components are required for the success of GSC.²³

The adsorption process involves diffusion of solute to the surface, adsorption at the surface, and diffusion from the surface.²⁴ The amount of substance adsorbed depends on the surface area of the adsorbent and the concentration of the substance in the carrier gas.

The adsorption isotherm is described by the Langmuir equation which assumes adsorbed molecules form only a monolayer

on the adsorbent:

$$p/(w/m) = \frac{1}{k_1 k_2} + \frac{p}{k_2}$$

where w is the weight of gas adsorbed by m grams of adsorbent at a gas pressure p . k_1 and k_2 are constants for a given system. $p/w/m$ is plotted against p to obtain the slope of the curve.

Not all systems behave in accordance with this equation. Adsorption isotherms for GSC are usually nonlinear and frequently convex. A greater percentage of solute is adsorbed from a less concentrated solution than from a more concentrated one; and as adsorption sites are saturated, adsorption approaches a limit.²⁵ Tailing (zone distortion, leading to the formation of long drawn-out peaks) is often attributed to nonlinear adsorption isotherms. When a weaker solution of the carrier gas and sample mixture is formed while passing through the column, it is retained more by the adsorbent and tails behind the stronger solution. As a result peaks in GSC often have a sharp front and an elongated tail. Tailing may also originate in the column as a kinetic effect related to adsorption-desorption from non-uniformly active adsorption sites (i.e. the rate of adsorption-desorption varies if the sites of an adsorbent are not equal in activity).²⁶

Plate height (HETP, sometimes abbreviated H) is often used in partially characterizing symmetrical and near-symmetrical

peaks. The equations which define H are an attempt to assess individual contributions to peak spreading by column parameters. Although the theoretical plate model itself (mentioned in the Introduction) is somewhat unrealistic in its description of chromatographic columns, the mathematical equations are justifiable and useful.

The plate-height equations formulated for GSC may be summarized by the following:

$$H = A' + B/v + C_g v + C_k v$$

$$\text{or}$$

$$H = \sum \frac{1}{1/A_i' + 1/C_{gi} v} + B/v + C_k v$$

where A' , the eddy diffusion term due to multiple paths between particles of stationary phase, is coupled with the C_g , gas phase resistance to mass transfer term in the latter equation. The subscript i refers to a plate-height component. B is the longitudinal diffusion term; v , the gas velocity (distance per unit time for "air" to pass through the column and be recorded as a peak). The equation for GLC is almost identical since most of the processes are so similar. The major difference is the replacement of the C_k (k=kinetic) mass transfer term for the kinetics of adsorption and desorption in GSC by the C_l (l=liquid) mass transfer term for the solute in the liquid phase.²⁷ The Van Deemter, Zuiderweg, and Klinkenberg equation reads for GLC:

$$H = \underbrace{2\lambda d_p}_A + \underbrace{2r\Delta/v}_B + C_g v + C_L v$$

where λ is the statistical irregularity of the packing, d_p is particle diameter of support for liquid phase, D_g denotes molecular diffusion in the gas phase and r is the labyrinth factor of the pore canals.²⁸

The basic approach to this theory is statistical. There is a mathematical theorem which states "for a group of independent statistical processes occurring simultaneously the total variance is the sum of the individual variances while the mean is the sum of the individual means."²⁹ The validity of simply adding the independent contributions to H of the various terms can be proven.³⁰

The object of the experimentalist in GC is to minimize H and therefore, peak spreading. A smaller peak width indicates more column efficiency; and often, but not necessarily, better resolution is the end result. If one can make the individual terms in the HETP equation as small as possible H will be at a minimum and most likely the best performance effected.

GSC and GLC require the same apparatus but the operating conditions necessary for the two systems differ in several ways. Adsorption partition coefficients are generally greater than solution partition coefficients. Consequently, retention times (time from sample injection to maximum peak height of eluted compound) or retention volumes (retention time multiplied by flow rate) are larger. Nonlinear partition isotherms are more common

in GSC than GLC and tailing is more prevalent except for low boiling materials. To approach more linear isotherms, the temperature is usually higher and the sample size smaller in GSC than in GLC. The results in GSC are usually less reproducible, since the column tends to change with use by deterioration or by adsorbing water. In GSC there is a greater chance for adsorbent-catalyzed reactions of the sample to take place. Also, active adsorbent columns must often be activated by heating for two to three hours before use.³¹

All these factors of GSC operation tend to favor GLC.

However, GSC offers two immediate potential advantages over GLC. Adsorption is capable of offering more selective characteristics than other retention mechanisms. As an example, isomers are sometimes easily separated in GSC due to the steric nature of the forces involved in the adsorption process. Another possible advantage of GSC is the probability that the C_k value in the HETP equation is smaller than the C_1 of GLC. J. Calvin Giddings, author of a book and numerous papers on GC, speculates that GSC may eventually provide the "ultimate" column if resistance to mass transfer in the gas phase C_g can be reduced to a negligible value.³² He proposes using low pressures and electromagnetic forces applied to an ionized carrier gas to provide the necessary propulsion for a reasonable carrier gas flow rate.³³

C. G. Scott, another noted author in this area of work,

suggests that GSC should be studied from its thermodynamic aspects. GSC provides one of the easiest means of estimating enthalpy, free energy, and thence entropy. The correlation of these factors in terms of their effects on column performance may eventually be obtained and a real breakthrough in scientific knowledge accomplished.³⁴

Applications of Gas Chromatography:

Presently Gas Chromatography is used extensively in both industrial and university research programs to identify the constituents of a mixture qualitatively by retention times, or quantitatively by calculating peak areas. Nondestructive separations of samples far too small for distillation and solvent extraction may be effected by this procedure. The sample size in analytical gas chromatography may be between 10^{-8} and 10^{-2} grams; however samples up to 100 grams have been separated by using large diameter columns in what is called preparative scale GC. A broad quantitative range is covered,³⁵ and the accuracy of GC is of the order of 1 percent of the amount of any substance separated. As a result the quantity of a trace component is determined with the same relative accuracy as that of a major component in a mixture. Usually the sensitivity of detectors can be altered by many powers of ten.³⁶ Another feature of this method is that it requires relatively inexpensive equipment and simple execution.

A separation may be effected in several minutes or several hours depending on the complexity of the mixture.

Often GC is supplemented by other identification methods such as nuclear magnetic resonance, infra-red and mass spectroscopy. For example, GC is used to separate the components of a mixture, and then a mass spectrum is drawn for each compound as it emerges from the column.³⁷

GC's worth to the scientist is not limited to isolating pure materials. This method provides information about physio-chemical quantities, such as vapor pressures, boiling points, latent heats, heats of solution and mixing, activity coefficients, free energies and entropies, interactions of solute solvent and adsorbent-adsorbate, and possibly diffusion rates in both gas and liquid phases.³⁸

EXPERIMENTAL

Equipment:

The chromatograph used was a Perkin-Elmer Model 154L equipped with a dual chamber thermistor thermal conductivity cell. The operation of this instrument was described previously in the section subtitled Apparatus. Helium was used as the carrier gas.

Sample:

Laboratory-grade materials were used without further purification. Sample size ranged from $\frac{1}{2}$ to 2 microliters.

Hamilton 10- and 50-microliter syringes were used to introduce the sample into the column.

Column Preparation:

Five different columns were prepared. First Quso F20 was poured into copper tubing (2-meter by $\frac{1}{4}$ -inch outside diameter). Then the silica was packed by vibrating and tapping the tubing on the floor. This is a standard technique for GC packing. When the tubing appeared filled with Quso, the two ends were plugged with glass wool. The column contained 2.84 grams of Quso. After packing, the column was bent into a U-shape and positioned in the chromatograph. The gas flow was started, and it was discovered that the gas did not pass through the column at a reasonable flow rate. This column of high resistance was rejected.

The next column was packed in the same manner using the same copper tubing. This time a mixture of sand and Quso (34 grams of sand to 1 gram of Quso) was poured into the column. It was noticed that the light, powdery Quso particles did not remain randomly distributed throughout the sand during the pouring. Instead they collected at the sides of the funnel and entered the column in loose clusters. As a result, the packing was not a mixture of sand and Quso, but a series of sand and then Quso deposits in the tubing. Since the object was to prepare a uniformly dispersed mixture of sand and Quso, this column was rejected.

Then 2.5 grams of Quso were added to 91.5 grams of sand and 9 ml. of water. The resulting thick, granular paste was stirred vigorously and allowed to dry overnight. The sand particles appeared to be coated with Quso and were introduced into the original copper tubing (1-meter in length) using the ~~same~~ packing technique (see first column description). The column contained 0.521 grams of Quso. Before use this column was activated by heating for six hours at 70°C. This column is designated column one.

The next column, called column two, was prepared by mixing 60.0 grams of Fluoropak 80, a non-polar chromatograph solid support produced by the Fluorocarbon Company of California, with 1.00 grams of Quso. The mixture was poured into the original U-shaped copper tubing. To insure tightness in packing, the tubing was tapped regularly. Column two was activated at least two hours at 100°C before use. It contained 0.213 grams of Quso.

Ninety grams of 60- to 80-mesh glass beads (Microbeads, Inc., Jackson, Mississippi) were mixed with a paste of 1.5 g Quso and 10 ml. of water. The Quso coated beads were dried two hours at 80°C, and this packing was used in stainless steel tubing, 2.03 meters by $\frac{1}{4}$ -inch outside diameter. The same technique was employed in packing this column as in the other four. However, due to the length of the column, two U-bends were made in the tubing. This column, column three, contained 0.787 grams of Quso. It was

The first thing I saw when I stepped out of the car was a vast, open landscape. The horizon was a straight line, and the sky was a pale blue. The air was still, and the sun was low in the sky, casting a warm glow over the scene. I felt a sense of peace and tranquility, as if I had found a hidden gem in a world of chaos. The landscape was a mix of rolling hills and open fields, with a few scattered trees and small buildings in the distance. It was a beautiful sight, and I knew that I had found a place where I could truly relax and enjoy the view.

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activated for two hours at 100°C.

Results and Discussion:

The data obtained from the three usable columns are presented in Tables I, II, and III. The tabulation shows the retention time (d_R) for each of the sample components and the operating conditions (temperature and flow rate) for each sample.

On all three columns when polar and steric factors are not controlling, the components of a sample were usually eluted in the order of lowest-to-highest boiling point. This occurrence is customary in GC. The lower the boiling point of a compound, the higher its vapor pressure. Therefore, at constant temperature, the low boiling component has a greater percentage of its initial concentration in the gas phase than a high boiling compound. Due to the fact that the low boiling compound spends less time adsorbed on the stationary phase, it will be eluted first. At higher temperatures more molecules of the sample components have a higher energy and remain ~~in~~ move to the gas phase (i.e. the concentration of sample in the carrier gas is increased). Consequently, retention times for the compounds are reduced.

Excellent resolution and good symmetrical peaks are produced for the mixture of pentane and heptane on column one at both 71°C and 67°C with a flow rate of 50 ml./min. As expected, a lower temperature, 67°C, resulted in increased d_R values.

components. For column two and three, the same sample was injected at a much lower temperature (43°C), although the flow rates for these columns were similar to column one (48 ml./min. to 50 ml./min.). The pentane peaks for columns two and three showed good symmetry while the peaks for heptane were slightly tailed. The better resolution and increased retention times obtained for the glass bead column are probably a result of greater length and more Quso present than in the fluoropak column.

Sample mixtures of pentane and cyclohexane were injected into both column two and three using identical conditions of 42°C and 30 ml./min. flow rate. Values of d_R were approximately twice as large for column three as for column two. With the longer glass beads column good resolution was obtained, whereas the two compounds were not completely separated on the fluoropak column.

In the separation of cyclohexane and cyclohexene, column three gave the most nearly symmetrical peaks and the best resolution. The conditions under which this sample was injected were 36°C and 50 ml./min. At 32°C and 40 ml./min. on column two, these two peaks were not completely separated, and the cyclohexene peak had a long drawn out tail. Although cyclohexane had a longer retention time on the fluoropak column than on the coated glass beads, the cyclohexene d_R on column two was smaller. It is suspected that the polarity of cyclohexene contributes to the forces of attraction between the adsorbent (which has a strong affinity for

polar compounds) and this component. With a longer column and more Quso, the retardation of cyclohexene is enhanced. On column one, the same sample mixture was injected at a column temperature of 67°C and a flow rate of 50 ml./min.. The peaks were resolved, but the cyclohexene peak tailing increased. It is interesting to note that in this particular case the same flow rate and about a 20° lower temperature resulted in d_R values (from the Quso and sand column) which were at least twice the magnitude of those for the longer glass beads column.

For a sample mixture of methylene chloride and chloroform passed through both columns one and two at the same temperature and flow rate (54°C and 43 ml./min.), the chromatograms were indistinguishable as far as a qualitative estimation of resolution and peak tailing. However, retention times were considerably larger for column one. This factor seems to favor the use of column two in separating this specific sample. In addition, the pentane peak (discussed in connection with the pentane-heptane sample) from column two is just as symmetrical as that from the Quso and sand column which was operating about 20° higher in temperature and 10 ml./min. faster in flow rate. Also, the columns gave almost identical retention times for this sample. It is surmised that the amount of Quso present in column two may be sufficient to separate a variety of sample mixtures that require a low temperature, or to perform rapid analyses. Of course the compound

suitable to these conditions (besides pentane, cyclohexane, chloroform, and methylene chloride) must be determined, but the data suggests possibilities in low boiling, nonpolar hydrocarbons.

When using the conditions specified in the tables for 1-chlorobutane and 2-chlorobutane, neither column one nor column two resolved this sample mixture. For column one, these conditions were varied several times and identical sample mixtures were injected for each new set of column parameters. It is possible that the first samples introduced covered some of the adsorption sites through irreversible adsorption so that d_R values for later samples were markedly reduced. As an example, at 66°C and 38 ml./min., the d_R was 10.50. A 12 ml./min. increase in flow rate has changed d_R values considerably. When 1- and 2-bromopropane were analyzed on column two and three, neither chromatogram showed resolution. Yet, with 1-bromopropane and 1-bromobutane, the chromatograms from all three column analyses had two easily distinguishable peaks. With the same temperature and flow rate parameters as column two, the glass beads column brought about better resolution.

It is not certain that Quso columns do not separate isomeric halides; it can only be said that optimum conditions may not have been chosen for the analyses. For resolving these substances, column parameters were probably very crucial factors.

Complete resolution of a mixture of benzene, toluene, and

xylene (para) was effected by column one at 120°C and 43 ml./min. At 130°C and 30 ml./min., column three gave three easily distinguishable peaks, which overlapped only slightly. With column two at the same flow rate and a lower temperature by 4°, the resolution was not as good. In this case the fluoropak column may require an even lower temperature for complete separation of this mixture. On the other hand, the amount of Quso in the column may be too small to bring about totally resolved peaks even at optimum conditions.

In the analysis of a benzene, toluene, and cyclohexane sample mixture, both columns two and three produced three discernable peaks with the same conditions. However, tailing on toluene is less and resolution better for column three. At 95°C, this sample on the glass beads column gives a chromatogram showing considerable tailing with both benzene and toluene.

A mixture of chloroform, toluene, and acetone was analyzed on columns one and three under conditions specified in the tables. Both chromatograms demonstrated zone distortion with toluene. Also, the chart drive for the recorder was allowed to run for at least 12 minutes (1-inch/minute) for these chromatograms. Within this time, an acetone peak did not appear. Similarly, pentanone and octanone produced no peaks within a 12 inch d_R when analyzed on columns one and three. At a temperature of 146°C (higher than that used for the other columns), column two gave one somewhat tailed

peak. Neither column two nor three resolved ortho- and para-xylene.

Of interest is the improvement in resolution obtained when analyzing gasoline on the glass beads column as compared to that obtained with column two at the same temperature and flow rate (see Tables II and III). Again optimum conditions for column two may not have been employed, but it is surmised that the glass beads column is more suitable to the separation of higher boiling hydrocarbons at high temperatures. This conjecture is based on the greater length and amount of Quso as well as the effectiveness of using glass beads as a support for a solid stationary phase.³⁹

The uniform spherical bead packing allows the gas to flow through the column more easily than if an irregular granular support such as sand or fluoropak is used. As a consequence, the A' and B terms in the HETP equation are smaller and efficiency is increased (i.e. peak spreading is reduced). Coating the beads with a solid adsorbent of high surface area provides a large surface area favorable to mass transfer. Generally, a liquid stationary-phase coating does not provide as much available surface area. In modified GSC, when a small amount of liquid phase was coated on the solid adsorbent-coated glass beads, the separation of polar and high boiling substances was achieved.⁴⁰ In view of this fact, it seems reasonable to suspect that Quso-coated glass beads with a liquid coating such as polyethylene glycol may be a very good and versatile column packing for separating these substances.

In an attempt to determine the reproducibility of the d_R values, column two was activated again for two hours at 100°C after remaining idle for one week. The sample mixture of 1-bromopropane and 1-bromobutane was injected at the same flow rate and a temperature 4° lower than in the original analysis. As expected, slightly longer retention times were obtained. If the column had deteriorated, it was not evident from the data. Of course, more samples (at conditions identical to those of the first analysis) should be separated on the column during a period of several months and the data compared. Time did not permit a complete investigation.

Conclusion:

The previous discussion was not intended to compare the columns prepared as to which is "the best," but rather to demonstrate the utility of Quso as a solid stationary phase in GSC. As already mentioned, the most favorable conditions for each column may not have been selected and tried. Instead, a general survey of operating conditions and sample mixtures for Quso columns was conducted. The data indicate that Quso is useful as a column packing for the separation of low-boiling hydrocarbons and non-polar substances.

In the past GSC with such solid adsorbents as silica gel, alumina, and activated carbon, has had widespread use as a

technique for separating permanent gases and hydrocarbons up to five or eight carbon atoms. With any of the three packing mixtures (Quso with sand, Quso with fluoropak, Quso on glass beads), the columns prepared gave excellent peaks for pentane, cyclohexane, and benzene. It seems reasonable to conjecture that these columns likewise will be useful for analyzing permanent gases and gaseous hydrocarbons. Even now, in view of the research already carried out, it can be said that the Quso -sand mixture offers an inexpensive simple form of packing for some qualitative GC analyses.

From the data collected, the applicability of Quso to GSC seems apparent and the area of study worthy of further investigation.

Proposals:

The following recommendations are made for future studies of Quso columns:

(1) Stainless steel tubing might be preferable to copper tubing for columns. Copper may possibly catalyze reactions on the packing.

(2) Fine mesh brass soldered to the tubing ends may give better efficiency results than glass wool plugs. These glass wool plugs may cause a greater pressure drop across the column.

(3) It would be advisable to collect the sample components eluted from the column and check to see if they have been altered

after passing through the column. This determination would possibly eliminate the suspicion that a sample mixture is reacting with the adsorbent.

(4) To reduce adsorbent activity, a smaller amount of Quso coating on the glass beads might possibly be investigated. Other research may be carried out with the fluoropak column. Liquid-coated fluoropak mixed with Quso could be studied as a column stationary phase.

(5) Experimental work with the use of hydrophobic Quso in GSC packing, instead of the hydrophilic, would be interesting.

(6) It is suggested that Quso F20 be investigated as a possible stationary phase for liquid-solid chromatography.

Table I. Retention Times; Column One
(1 inch/minute)

<u>Sample</u>	<u>Retention Time (in.)</u>	<u>Temperature (°C)</u>	<u>Flow Rate (ml/min)</u>
Pentane	0.75, 0.80	71, 67	50, 50
Heptane	2.25, 2.60	71, 67	50, 50
Cyclohexane	1.30	67	50
Cyclohexane	2.10	67	50
Cyclohexene	3.80	67	50
Methylene chloride	2.30, 1.20	54, 100	43, 35
Chloroform	3.50, 1.20	54, 100	43, 35
1-Chlorobutane	10.50, 8.50	66, 60	38, 38
2-Chlorobutane	10.50, 8.50	66, 60	38, 38
1-Chlorobutane	3.40, 3.50	76, 66	44, 50
2-Chlorobutane	3.40, 3.50	76, 66	44, 50
1-Bromopropane	1.50	100	35
1-Bromobutane	3.00	100	35
Benzene	1.85	100	35
Toluene	5.10	100	35
Benzene	1.40, 1.80	120, 100	43, 43
Toluene	2.30, 3.00	120, 100	43, 43
Xylene (para)	4.80, 7.00	120, 100	43, 43
Chloroform	1.40	98	35
Toluene	4.70	98	35
Acetone	No peak*	98	35
Acetone	No peak*	100	35
2-Pentanone	No peak*	111	40
2-Octanone	No peak*	111	40

* No peak (i.e. no peak appeared within a retention time of 12 inches).
This definition applies to Tables II and III also.

Table II. Retention Times; Column Two
(1 inch/minute)

<u>Sample</u>	<u>Retention Time (in.)</u>	<u>Temperature (°C)</u>	<u>Flow Time (ml/ min)</u>
Pentane	0.90, 0.85	43, 45	48, 31
Heptane	4.60, 2.50	43, 45	48, 31
Pentane	1.10	50	30
Heptane	4.10	50	30
Cyclohexane	1.50	50	30
Pentane	0.90, 0.70	42, 42	30, 30
Cyclohexane	1.40, 1.10	42, 42	30, 30
Cyclohexane	0.80	82	40
Cyclohexene	1.40	82	40
Methylene Chloride	1.40	54	43
Chloroform	1.45	54	43
Carbon tetrachloride	1.50	49	31
Methylene Chloride	2.00	49	31
Chloroform	2.30	49	31
1-Chlorobutane	1.10	85	33
2-Chlorobutane	1.10	85	33
1-Bromopropane	1.50	63	35
2-Bromopropane	1.50	63	35
1-Bromopropane	1.10, 1.15, 2.55	89, 85, 69	33, 33, 40
1-Bromobutane	1.70, 1.95, 5.10	89, 85, 69	33, 33, 40
Benzene	0.80	138	30
Toluene	1.40	138	30
Cyclohexane	0.50	138	30
Benzene	1.00	126	30
Toluene	1.40	126	30
Xylene (para)	2.80	126	30
Xylene (para)	1.50	143	30
Xylene (ortho)	1.50	143	30
Acetone	1.60	154	27
Water	1.40	154	27
2-Pentanone	2.40	146	30
2-Octanone	No peak	146	30
Gasoline (3 distinguishable peaks)	0.70, 0.90, 1.40	105	35

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99	99	99	99	99
100	100	100	100	100

Table III. Retention Times; Column Three
(1 inch/minute)

<u>Sample</u>	<u>Retention Time (in.)</u>	<u>Temperature (°C)</u>	<u>Flow Rate (ml/min.)</u>
Pentane	1.30	43	48
Pentane	1.60	45	31
Heptane	6.30	45	31
Pentane	1.60	42	30
Cyclohexane	3.60	42	30
Cyclohexane	0.70, 0.70	86, 108	50, 27
Cyclohexene	1.60, 1.30	86, 108	50, 27
Carbon tetrachloride	2.50, 3.00	49, 42	31, 30
Methylene Chloride	2.50, 3.35	49, 42	31, 30
Chloroform	4.20, 5.90	49, 42	31, 30
1-Bromopropane	3.00, 3.60	60, 68	35, 30
2-Bromopropane	3.00, 3.60	60, 68	35, 30
1-Bromopropane	2.20, 2.25	85, 85	33, 50
1-Bromobutane	3.50, 4.00	85, 85	33, 50
Benzene	1.20, 2.60	138, 95	30, 32
Toluene	2.00, 5.65	138, 95	30, 32
Cyclohexane	0.70, 1.00	138, 95	30, 32
Benzene	1.70	130	30
Toluene	2.50	130	30
Xylene (para)	4.20	130	30
Xylene (para)	2.00	135	50
Xylene (ortho)	2.00	135	50
Xylene (para)	1.90	137	50
Xylene (meta)	1.90	137	50
Chloroform	1.10	110	30
Toluene	3.60	110	30
Acetone	No peak	110	30
Ethyl Acetate	No peak	90	50
2-Pentanone	No peak	137	50
2-Octanone	No peak	137	50
Gasoline (3 components distinguished)	1.00, 1.20, 1.40, 1.60, 1.80, 2.30, 2.70, 3.70	110	27
Gasoline (7 peaks distinguished)	1.40, 1.80, 1.90, 2.10, 3.00, 4.80, 8.00	105	35

Table IV. Boiling Points and Molecular Weights

<u>Compound</u>	<u>B.P. (°C)</u>	<u>M.W. (grams)</u>
Pentane	35-36	72.15
Methylene Chloride	40-41	84.94
Acetone	56.5	58.08
Isopropyl bromide	59-60	123.00
Chloroform	61.26	119.39
2-Chlorobutane	68	92.57
1-Bromopropane	70.9	123.00
Carbon tetrachloride	76.8	153.84
1-Chlorobutane	78	92.57
Benzene	80.09	78.11
Cyclohexane	81.4	84.16
Cyclohexene	83	82.14
Heptane	98	100.20
1-Bromobutane	101.6	137.03
2-Pentanone	101.7	86.13
Toluene	110.6	92.13
Xylene (para)	138.35	106.16
Xylene (meta)	139.10	106.16
Xylene (ortho)	144.4	106.16
2-Octanone	173.5	128.21

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